

tural analysis to systems of this type can yield unique *dynamic* models of chemically significant molecular transformations.

Acknowledgments. This research was made possible by the support of the UCLA Research Committee, the UCLA Campus Computing Network, and the UCLA President's Undergraduate Research Fellowship Program. We also wish to thank Mr. Hsi-Chao Chow for his help in the initial stages of this work.

Supplementary Material Available: A listing of all observed and calculated structure factor amplitudes (45 pages). Ordering information is given on any current masthead page.

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Radicals and Scavengers. 7. Diffusion Controlled Scavenging of Phenyl Radicals and Absolute Rate Constants of Several Phenyl Radical Reactions¹

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Abstract The thermal decomposition of phenylazotriphenylmethane (PAT) has been studied in mixtures of benzene and chlorobenzene with mineral oil in the presence of the phenyl radical scavengers I_2 , CBr_4 , $BrCCl_3$, and Me_2CHI . Greater than 90% yields of halobenzenes as scavenging products are observed at all concentrations in pure aromatic solvents, as previously reported. In viscous mixtures, however, high scavenging yields are found only at high scavenger concentrations, while at low scavenger concentrations yields fall as low as 32%. Substantial concomitant increases in benzene yield (in chlorobenzene mixtures) occur. Substitution of *n*-heptane for mineral oil almost entirely eliminates the drop in scavenging yields. These observations are readily explained by postulating that the reactions of scavengers with phenyl radicals are nearly diffusion controlled in benzene or chlorobenzene. An order of magnitude or greater increase in viscosity then decreases the diffusion rate constants significantly, allowing other reactions, particularly formation of benzene by H abstraction from mineral oil, to compete. Alternative models, e.g., complexing of scavengers with PAT or cage scavenging, do not explain the difference in behavior of mineral oil and *n*-heptane. Two predictions of this model have been fulfilled: first, the relative reactivities of scavengers toward phenyl radicals approach unity at high viscosities; second, the rate constant, k_H^{app} , for $Ph\cdot + R-H \rightarrow Ph-H + R\cdot$ ($R-H =$ mineral oil) can be calculated by assigning to the I_2 and CBr_4 scavenging reactions the diffusion limited value calculated via the combined Wilke-Chang and von Smoluchowski equations. The calculated value of k_H decreases with rising viscosity to a plateau value which is essentially the same for both scavengers, viz., $k_H = 3.3 \pm 0.7 \times 10^5 M^{-1} s^{-1}$. Other rate constants are calculated from competition studies. The rate constants estimated by Starnes and by MacLachlan and McCarthy, and extrapolated from gas phase results at $\sim 300^\circ C$ of Duncan and Trotman-Dickenson are in poor agreement with the present values. The value for phenyl with O_2 is found to be virtually identical with that for CBr_4 ; thus the reason for the "small" ratio of k_{O_2}/k_{CCl_4} reported by Russell and Bridger, and the *apparent* unreactivity of phenyl toward O_2 , is the high reactivity of phenyl toward CCl_4 and other solvents, not a low reactivity toward O_2 . The selectivity-reactivity relationship is not obeyed by several radicals, including phenyl.

The phenyl radical and its substituted analogs have been extensively studied in solution. Several means of generating them are known;³ they have been shown to add to aromatic rings,³ double bonds,³ and trivalent phosphorus,⁴ and sometimes probably to divalent sulfur,⁵ as well as to abstract the

univalent atoms H, Cl, Br, and I,³ but to react inefficiently with O_2 in CCl_4 .⁶ Their relative reactivities toward a variety of substrates have been determined^{7,8} and compared with those of alkyl, alkoxy, and halogen radicals.⁷

In contrast to numerous alkyl radicals⁹ and the *tert*-butoxy

Table I. Yields of Tetraphenylmethane from PAT Decomposition^a in Benzene at 80 °C

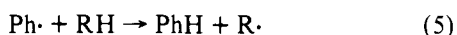
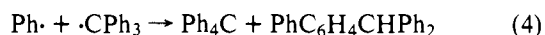
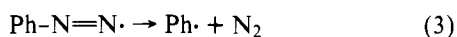
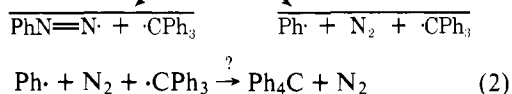
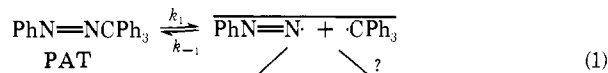
[PAT] ₀ , M	% yield of Ph ₄ C	Mp of Ph ₄ C, °C ^b
0.595	2.0	277–279
0.297	2.9 ^c	265–273
0.148	2.2	278–284
0.029 ₇	0.26	279–281

^a For 2 h. ^b Lit. 281–282 °C.³⁶ ^c Probably too high, since product was impure.

radical,¹⁰ however, absolute rate constants for reactions of phenyl radicals in solution remain unknown.^{3d} Several estimates have been attempted,¹¹ and constants have been reported for the gas phase at ~300 °C.¹² The lack of suitable chain reactions involving the phenyl radical is largely responsible for our ignorance of rate constants for its reactions, since the rotating sector method could not be applied. However, Hoz and Bunnett¹³ have found evidence that the reaction of iodobenzene with diethyl phosphite ion in Me₂SO involves free phenyl radicals. If, as seems likely, the initiation and termination steps are such that the addition of phenyl radical to the ion is rate limiting, a rotating sector study to determine that rate constant may be feasible.

There are indications that the reactivity of the phenyl radical may rival or exceed that of *tert*-butoxy, for which H-atom abstraction from toluene at 25 °C has recently been assigned the rate constant $0.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.^{10b} The two radicals have similar selectivities toward aliphatic and benzylic C–H bonds.⁷ Like *tert*-butoxy, phenyl does not appear to dimerize to a significant extent in solution;¹⁴ in the case of *tert*-butoxy this is due to an extremely low steady-state concentration, which is in turn due to its rapid destruction by H-atom abstraction from solvent (as well as competing β scission in less reactive solvents).¹⁵ Indeed, coupling reactions of *tert*-butoxy radicals are in general observed only as cage processes;^{15,16} the only exceptions are coupling with persistent radicals such as galvinoxyl and triphenylmethyl,¹⁷ which can exist at relatively high concentrations. Recent studies of the decomposition of phenylazotriphenylmethane in phosphite ester solvents,⁴ in di-*tert*-butyl sulfide,⁵ and with scavengers in aromatic solvents¹⁸ indicate that the same may be true of phenyl radicals.

We therefore included the phenyl radical in a program to test a competition technique for determining absolute rate constants, which has previously been applied to the *tert*-butoxy radical.^{10b} The reaction of interest, e.g., H abstraction (reac-



tion 5), is allowed to compete with a diffusion controlled reaction, for example a radical coupling such as reaction 4. Diffusion control of reaction 4 would be demonstrated by observing it as a cage process, reaction 2, utilizing if necessary the technique of increasing solvent viscosity.¹⁶ The coupling rate constant, k_4 , would be calculated via eq 6

$$k_4 = fk' \quad (6)$$

Table II. Decomposition of PAT with I₂ in Benzene–Mineral Oil at 70 °C

Mineral oil, vol %	η , cP ^b	% yield of PhI ^a			
		0.002 ^c / 0.01 ^d	0.01 ^c / 0.03 ^d	0.009 ^c / 0.08 ^d	0.024 ^c / 0.14 ^d
0	0.358	96	102	104	98
30	0.633	74	96	102	98
50	1.045	55	73	96	96
70	2.18	46	61	94	99
80	3.53	41	65	73	97
90	7.67	41	49	69	

^a Average deviation = $\pm 3\%$. ^b For 100% mineral oil at 70 °C, $\eta = 16.3$ cP. ^c [PAT]₀, M. ^d [I₂]₀, M.

where f = fraction cage effect; k' = diffusion limited second-order rate constant. Finally, the rate constant of reaction 5, k_H , would be calculated from competition data. The decomposition of phenylazotriphenylmethane (PAT), eq 1, was chosen as the source of phenyl radicals because these are evidently produced quantitatively. Thus, >90% yields of iodobenzene were observed in toluene at 50 and 70 °C in the presence of 0.03–0.12 M I₂.¹⁹

In short, our efforts to demonstrate diffusion control of reaction 4, or its operation as the cage reaction 2,²⁰ were unsuccessful. Hence k_H could not be determined from competition studies involving reactions 4 and 5. During our studies, however, we observed that the efficiencies of scavengers toward phenyl radicals are jointly dependent on scavenger concentration and viscosity. From this critical clue the determination of rate constants quickly emerged. We now describe our scavenger studies and show how we have succeeded in determining k_H and a variety of additional rate constants.

Results

Yields of Tetraphenylmethane. Tetraphenylmethane was first prepared by Gomberg²² from the thermal decomposition of PAT; the yield in benzene was reported to be ~2–5%. Subsequently, Fu and Bentrude⁴ showed that only some 0.5% each of tetraphenylmethane and 4-biphenyldiphenylmethane are formed in neat trimethyl phosphite, which they also showed to be ~100 times as efficient a scavenger of phenyl radicals as CCl₄. Pryor and his collaborators¹⁸ showed that 1.5 and 0.5% yields of those two compounds, formed in CCl₄ at 60 °C, decrease to 0.7 and 0.3%, respectively, when 0.1 M I₂ is added.

To determine whether tetraphenylmethane in benzene originates from cage or bulk reaction, reaction 2 or 4, we decomposed PAT at different concentrations in benzene, isolating tetraphenylmethane by distillation. The yield was a function of concentration of PAT, as shown in Table I, a fact consistent with reaction 4 as its major source, or with a combination of reaction 4 and some induced decomposition. That is, at higher initial PAT concentrations, triphenylmethyl attains a higher concentration⁵ and is more efficient at scavenging bulk phenyl radicals, or, phenyl radicals attack PAT more frequently. Pryor et al.¹⁸ report a study by ESR of PAT decomposition which shows that trityl radicals reach a maximum concentration after two half-lives, decreasing slowly thereafter and persisting for months.

All these results place an upper limit of 0.5–1.0% on the cage effect in nonviscous solvents. A cage effect of 0.5–1.0% is not likely to be increased to the 10–20% range even by a 50-fold increase in viscosity.¹⁶ Indeed, we attempted to determine the yield of tetraphenylmethane in mixtures of benzene and mineral oil by column chromatography, but were unable to isolate it in more than trace amounts. Scavenger studies to be reported in this paper have led us to believe that indeed virtually no te-

Table III. Decomposition of PAT in Benzene–Mineral Oil with CBr₄ at 45 and 70 °C

Mineral oil, vol %	Viscosity, η , cP			% yield of PhBr, 70 °C			% yield of PhBr, 45 °C		
	70 °C	45 °C	45 °C ^a	0.0092 ^b /	0.0095 ^b /	0.0095 ^b /	0.01 ^b /	0.01 ^b /	0.009 ^b /
				0.03 ^c	0.06 ^c	0.20 ^c	0.06 ^c	0.20 ^c	0.50 ^c
0	0.358	0.462		90	102	100	99	99	101
20		0.644					92	86	99
30	0.633			87	83	97			
40		1.03					80	92	97
50	1.045			69	79	100			
60		2.02					84	79	98
70	2.18	3.11		60	64	90	59	77	96
80	3.53	5.58		55	52	70	54	67	95
87			9.85						96 ^a
90	7.67	12.08	12.7		37	69	47	61	94 ^a
92.5			15.7						87 ^a
95			19.5						91 ^a

^a In chlorobenzene–mineral oil; [PAT]₀, 0.019 M. ^b [PAT]₀, M. ^c [CBr₄]₀, M.

Table IV. Decomposition of PAT with BrCCl₃ at 70 °C and 2-Iodopropane at 45 °C

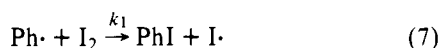
Mineral oil, vol %	η , cP, 70 °C	% yield of PhBr, ^a 70 °C		η , cP, 45 °C	% yield of PhI, ^b 45 °C, 0.017 ^c /0.10 ^e
		0.0093 ^c /0.03 ^d	0.023 ^c /0.28 ^d		
0	0.358	80	100	0.597	89
20	0.519	73	96	0.829	84
40	0.812	62	86	1.29	80
60	1.39	55	83	2.41	69
70	2.18	43	87	3.63	68
80	3.53	40	82	6.32	68
90	7.67	32	75	12.75	60
95				19.5	58

^a In benzene–mineral oil; for 100% mineral oil at 70 °C, $\eta = 16.3$ cP. ^b In chlorobenzene–mineral oil. ^c [PAT]₀, M. ^d [BrCCl₃]₀, M. ^e [i-PrI]₀, M.

traphenylmethane was present in these viscous mixtures. The small cage effect most likely means that the phenyldiazenyl radical loses nitrogen more slowly than the cage dissipates. As a result, the method outlined in the introduction cannot be used for determining k_{H} for phenyl radicals from PAT.

Scavenger Studies. A. Iodine. To establish with greater certainty the absence of cage reaction 2, we initiated an extensive study of scavenging which forms the major subject of this paper. If viscosity significantly increased the contribution of a cage reaction, the yields of scavenged product from efficient scavengers; e.g., I₂, carbon tetrabromide, bromotrichloromethane, and isopropyl iodide, should decrease.

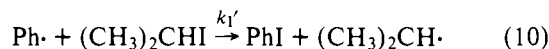
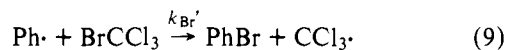
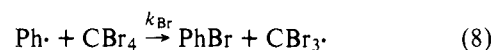
Table II records results for iodine at 70 °C. Although the iodobenzene yields fall with increasing viscosity at low initial iodine concentrations, the decreases vary with iodine concentration, and they disappear entirely at [I₂]₀ = 0.14 M.



That is, iodine is completely efficient, but only at quite high concentrations. By contrast, Waits and Hammond²³ found both iodine and bromine in chlorobenzene to be completely efficient at trapping free 1-cyanocyclohexyl radicals in the range 3×10^{-5} to 0.1 M. The present results make clear that complete efficiency in trapping phenyl radicals will not be achieved in benzene much below [I₂]₀ = 0.01 M.

B. Carbon Tetrabromide. Yields of bromobenzene from PAT decomposition in the presence of dilute CBr₄ show considerable decreases with viscosity at both 45 and 70 °C, as shown by Table III. At 0.20 M scavenger at 70 °C, however, the decrease is clearly evident only at 80 and 90% mineral oil, while at 0.50 M scavenger (at 45 °C) all yields are above 90%, within experimental error. These results mimic those with iodine, except that CBr₄ appears to be a less efficient scavenger, requiring a higher concentration for complete efficiency.

C. Bromotrichloromethane and Isopropyl Iodide. Yields of bromobenzene and iodobenzene, respectively, in the presence of each of these scavengers are listed in Table IV. Again decreases in yield of halobenzene with increasing mineral oil concentration are evident, even at rather high scavenger concentrations.



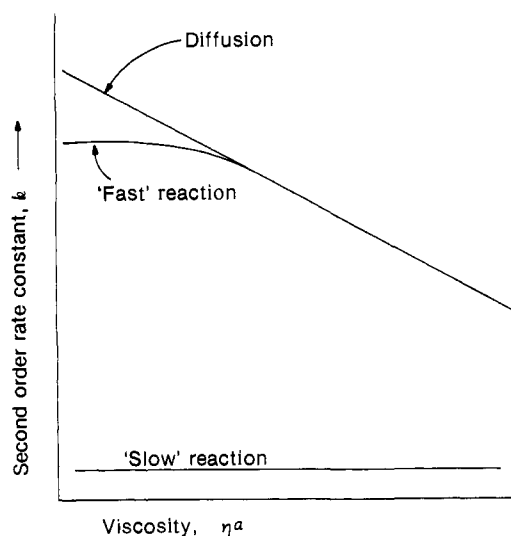
With bromotrichloromethane the decreases again are smaller, the more concentrated the scavenger. Both scavengers are less efficient than CBr₄.

Interpretation of Scavenging Results. The same pattern is shown qualitatively by all four scavengers, that is, high efficiency only at high scavenger concentrations in viscous solutions. Efficiencies in the 90–100% range at all viscosities imply that PAT has such a small cage effect, eq 2, that it increases to <10% at high viscosity. We must again conclude that our proposed method of determining rate constants is not viable.

Cause of Scavenger Inefficiency at High Viscosities. It is expected that low halobenzene yields are caused by competition with the solvent, i.e., by H abstraction (reaction 5) and/or aromatic phenylation. Indeed, experiments detailed below using chlorobenzene–mineral oil mixtures in place of benzene–mineral oil as solvent allowed us to observe substantial yields of H-abstraction product, benzene (cf. Tables XII and XIII). The question remains, however, whether the effective competition by solvent, presumably mineral oil, is due entirely to the rapidity of reaction 5 or to an additional cause. To in-

Table V. Decomposition of PAT with CBr₄ in Benzene-Heptane

% heptane in benzene	% yield of PhBr ^a			
	[CBr ₄] ₀ , 0.06 M		[CBr ₄] ₀ , 0.20 M	
	At 45 °C	At 70 °C	At 45 °C	At 70 °C
0	102	102	97	100
20	97	87	99	95
40	94	87	94	93
60	89	89	97	95
70	93	102	99	96
80	81	93	97	94
90	88	83	103	100

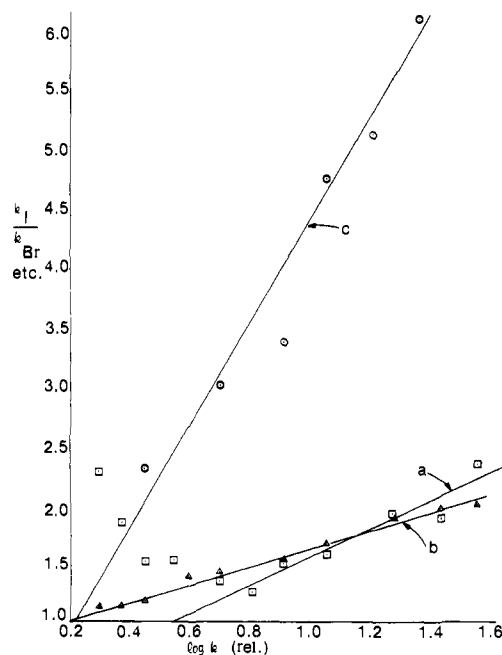
^a [PAT]₀, 0.0095 M.**Figure 1.** Relation of second-order rate constants and viscosity near and below diffusion limit; empirical constant *a* chosen to give linear plot for diffusion rate constant.

investigate this question, we repeated four series of CBr₄ experiments using *n*-heptane in place of mineral oil; Table V records the results. (A similar series with I₂ could not be carried out because of the low solubility of I₂ in *n*-heptane.) The results should be the same if the only important factor is C-H bond reactivity. The available evidence (vide infra) indicates that mineral oil, like *n*-heptane, contains no tertiary hydrogens.

To our surprise and eventual pleasure, significant decreases in bromobenzene yield with increasing proportions of heptane were *not* observed, even at 0.06 M CBr₄. Evidently the viscosity of mineral oil plays the crucial role in making scavengers inefficient toward phenyl radicals. To explain this, it is necessary to postulate that the scavenging reactions (7 and 8) have rates that are diffusion limited or very nearly so in benzene. As viscosity increases, their rates eventually *decrease*. The rate of H abstraction (eq 5), on the other hand, is probably well below the diffusion limit, and hence is unaffected by viscosity. Instead, reaction 5 consumes an increasing fraction of phenyl radicals as viscosity increases. The effects of viscosity on specific rates are illustrated in Figure 1.

Tests of Diffusion Control Hypothesis. The diffusion control hypothesis has been subjected to two experimental tests, in which the predicted results have been observed; the second test leads to an estimate of *k*_H, the rate constant of H abstraction, reaction 5, R-H = mineral oil.

1. Viscosity and Relative Reactivities of Scavengers. The first test is based upon the fact that at high viscosities the relative reactivities of two very efficient scavengers should approach unity, even if they differ from unity by twofold or more at low viscosity. As seen in Figure 1, the rate constants for reaction

**Figure 2.** Selectivities of phenyl radical toward scavenger pairs vs. *k'*(rel) (decreasing *log k'*(rel) corresponds to *increasing* viscosity): (a) □, *k*₁/*k*_{Br}, I₂ vs. CBr₄ (cf. Table VI, run 2); (b) △, *k*_{Br'}/*k*_{1'}, BrCCl₃ vs. Me₂CHI (cf. Table VII); (c) ○, *k*_{Br}/*k*_{1'}, CBr₄ vs. Me₂CHI (cf. Table VII). (Note that Tables VI and VII are supplementary material.)

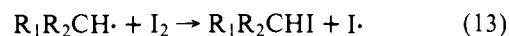
of two scavengers with the same radical will become identical with a "physical" rate constant, the diffusion limited one. I₂ and CBr₄ were therefore allowed to compete for the radicals from PAT, and *k*₁/*k*_{Br} calculated from the halobenzene yields via eq 11. Since the solubilities of scavengers in mineral oil limited their concentrations to values not much greater than that of PAT, the average I₂ concentration given by eq 12 was employed.

$$k_1/k_{Br} = \frac{[PhI][CBr_4]}{[PhBr][I_2]_{av}} \quad (11)$$

$$[I_2]_{av} = [I_2]_0 - [PhI]/2 \quad (12)$$

No correction was applied to the concentration of CBr₄, the products from which, CHBr₃ or Br₃C-CPh₃, should have similar scavenging ability toward phenyl. Similar experiments were also carried out using isopropyl iodide and either CBr₄ or BrCCl₃, rate constants for which are denoted *k*_{1'}, *k*_{Br}, and *k*_{Br'}, respectively. Relative rates were calculated by relations analogous to eq 11 using uncorrected scavenger concentrations.

The resulting relative rates are presented in Figure 2, as plots vs. *log k'*(rel), an inverse function of *η*: *k'*(rel) = calcd *k'*/calcd *k'* for 100% mineral oil. Dramatic decreases in all three ratios occur, as predicted. For *k*₁/*k*_{Br} above ~70% mineral oil, however, the ratio increases again. The increase might result from regeneration of I₂, but it was shown spectrophotometrically that, after several half-lives in 90% mineral oil-10% chlorobenzene, [I₂] was substantially *less* than required by the yield of iodobenzene. Consumption of I₂ by iodination of mineral oil via H abstraction (eq 5), followed by reaction 13



explains this fact. The secondary alkyl iodide produced is of a type known²⁴ to be good scavengers of phenyl radicals (cf. isopropyl iodide), and would thus raise the iodobenzene yield. High *k*₁/*k*_{Br} values should result.

Clearly, then, the increases in *k*₁/*k*_{Br} in very viscous media are an artifact, but the decreases in this ratio and the other two

Table X. Calculation of k_H from PAT Decomposition with CBr_4 in Chlorobenzene–Mineral Oil at 45 °C

Vol %	Mineral oil		η , cP	[PhH], M	[PhBr], M	Rate constants, $\text{M}^{-1} \text{s}^{-1}$	
	[C–H], M^a					$10^5 k_H^{\text{app} b}$	$10^{-9} k_{\text{Br}}^c$
Run 1 ^d							
10	12.3		0.694	0.00172	0.0248	44.7	
20	24.6		0.829	0.00185	0.0234	22.3	
30	36.9		1.03	0.00241	0.0221	16.9	
50	61.5		1.73	0.00441	0.0204	14.0	
60	73.8		2.41	0.00527	0.0207	9.87	
70	86.1		3.63	0.00565	0.0197	6.82	
80	98.4		6.32	0.00743	0.0177	5.41	
90	110.7		12.74	0.00906	0.0144	4.07	
Run 2 ^{e,f}							
20	24.6		0.829	0.00082	0.0194	14.9	3.83
30	36.9		1.03	0.00134	0.0185	14.2	3.37
40	49.2		1.29	0.00159	0.0182	10.6	3.72
50	61.5		1.73	0.00198	0.0175	9.14	3.58
60	73.8		2.41	0.00257	0.0168	7.41	3.18
70	86.1		3.63	0.00301	0.0163	5.49	3.08
75	92.2		4.72	0.00360	0.0155	5.13	2.61
80	98.4		6.32	0.00407	0.0142	4.62	2.26
83.3	102.3		7.74	0.00456	0.0143	4.22	2.12
86.7	106.7		9.85	0.00484	0.0134	3.76	1.95
90	110.7		12.74	0.00447	0.0127	2.85	2.08
92.5	113.8		15.70	0.00548	0.0112	3.20	1.54
95	116.8		19.48	0.00598	0.0109	2.96	1.41

^a Molar concentration of C–H bonds. ^b Calculated via eq 14. ^c Calculated via eq 17. ^d $[\text{PAT}]_0$, 0.026 M; $[\text{CBr}_4]_0$, 0.040 M, and this value was used in computing k_H ; cf. text. ^e $[\text{PAT}]_0$, 0.0207 M; $[\text{CBr}_4]_0$, 0.050 M, used for computing k_H . ^f In 100% chlorobenzene, $k_{\text{Br}} = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, extrapolated via plot of $1/k_{\text{Br}}$ vs. η .

Table XI. Calculation of k_H from PAT Decomposition with I_2 in Chlorobenzene–Mineral Oil at 45 °C^b

Vol %	Mineral oil		Viscosity, η , cP	[PhH], M	[PhI], M	Rate constants, $\text{M}^{-1} \text{s}^{-1}$	
	[C–H], M^a					$10^{-5} k_H^{\text{app} c}$	$10^{-9} k_1^d$
20	24.6		0.829	0.00029	0.0193	4.57	13.4
30	36.9		1.03	0.00043	0.0191	3.81	13.4
40	49.2		1.29	0.00069	0.0186	3.95	11.2
50	61.5		1.73	0.00102	0.0185	4.03	9.05
60	73.8		2.41	0.00152	0.0175	3.77	6.80
70	86.1		3.63	0.00224	0.0166	3.54	5.05
75	92.2		4.72	0.00274	0.0159	3.18	4.20
80	98.4		6.32	0.00328	0.0131	3.78	2.98
83.3	102.3		7.74	0.00358	0.0126	3.55	2.72
86.7	106.7		9.85	0.00427	0.0118	3.56	2.21
90	110.8		12.74	0.00459	0.0114	3.09	2.05
92.5	113.8		15.70	0.00465	0.0112	2.59	2.04
95	116.8		19.48	0.00472	0.0114	2.12	2.10

^a Molar concentration of C–H bonds. ^b $[\text{PAT}]_0$, 0.0196 M; $[\text{I}_2]_0$, 0.050 M. ^c Calculated via eq 14. ^d Calculated via eq 17; in 100% chlorobenzene, $k_1 = 15.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, extrapolated via plot of $1/k_1$ vs. η .

ratios reflect the onset of diffusion control. The test is successful, and the scavenging rate constants must all be near the diffusion limit.

2. Effect of Viscosity on Scavenger–Solvent Competition. Absolute Rate Constant k_H . The second test involves the competition for phenyl radicals between scavengers (reaction 7, etc.) and mineral oil (H abstraction, reaction 5) in chlorobenzene–mineral oil mixtures. Test values of k_H , or k_H^{app} , are calculated via eq 14

$$k_H^{\text{app}} = k' \left(\frac{\text{yield of PhH}}{\text{yield of PhX}} \right) \left(\frac{[\text{scavenger}]}{[\text{C–H}]} \right) \quad (14)$$

under the assumption that the scavenging rate constants k_7 , etc., are equal to the diffusion limited value. Since this assumption evidently becomes true at higher viscosities, a plot of k_H^{app} vs. viscosity should reach a plateau value, k_H^{lim} , at high viscosity. If the predicted plateau is observed, not only is the explanation of scavenger behavior vindicated, but k_H^{lim}

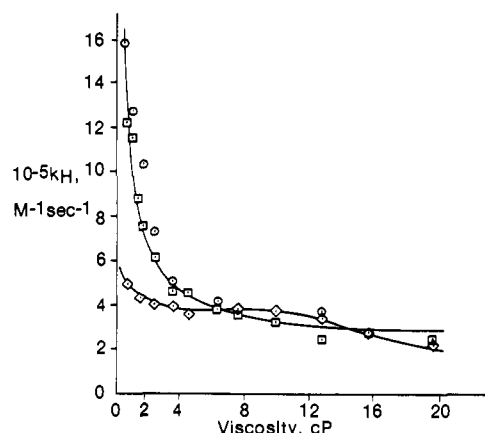


Figure 3. Determination of k_H via scavenger–mineral oil competition, using eq 14: \circ , CBr_4 (cf. Table X, run 1); \square , CBr_4 (cf. Table X, run 2); \diamond , I_2 (cf. Table XI).

Table XII. Relative Rates of Phenyl Radical Reactions at 45 °C

Solvent	[PAT] ₀ , M	Reactants and concn, M		Products and concn, M		Relative rate ^a	
						Obsd	Mean
PhCl + <i>c</i> -C ₆ H ₁₂	0.020	PhCl	<i>c</i> -C ₆ H ₁₂ ^b	C ₁₂ H ₉ Cl ^c	PhH	k_H/k_{PhCl}	
	0.020	9.83	0.0	0.0186	0.0008	0.259	0.251 ± 0.008
	0.020	7.85	22.5	0.0117	0.0094		
0.020	5.89	45.0	0.0070	0.0137	0.244		
PhCl + mineral oil	0.020	PhCl	Mineral oil ^b	C ₁₂ H ₉ Cl ^c	PhH	k_H/k_{PhCl}	
		5.89	49.2	0.00543	0.0121	0.250	0.250
PhCl + <i>c</i> -C ₆ H ₁₂	0.020	PhCl	<i>c</i> -C ₆ H ₁₂ ^b	<i>o</i> -C ₁₂ H ₉ Cl ^c	<i>p</i> -C ₁₂ H ₉ Cl ^c	k_{ortho}/k_{para}	
		9.83	0.0	0.0112	0.0074	1.58	1.68 ± 0.07
		0.020	7.85	22.5	0.0075	0.0042	
0.020	5.89	45.0	0.0044	0.0026	1.69		
PhH + CCl ₄	0.045	PhH	CCl ₄	Ph ₂	PhCl	k_{Cl}/k_{PhH}	
		5.63	5.24	0.00585 ^d	0.0302 ^d	5.60 ± 0.25 ^d	5.60 ± 0.25
PhH + PhCl	0.035	PhH	PhCl	Ph ₂	C ₁₂ H ₉ Cl ^c	k_{PhCl}/k_{PhH}	
		5.63	4.82	0.0120 ^e	0.0132 ^e	1.28 ± 0.03 ^e	1.28 ± 0.03 ^f
Benzene	0.022	I ₂	CBr ₄	PhI	PhBr	k_1/k_{Br}	
		0.40	0.40	0.0149 ^d	0.00717 ^d	2.08 ± 0.07 ^d	2.08 ± 0.07
Benzene	0.020	CBr ₄	<i>i</i> -PrI	[PhBr]/[PhI]		$k_{Br}/k_{I'}$	
		0.050	0.066	5.18 ^e	6.85 ± 0.7 ^e	6.0 ± 1.0	
CCl ₄	0.020	0.0806	0.490	0.85	4.85		
		0.0800	0.488	0.685 ^e	4.18 ± 0.15 ^e	4.2 ± 0.2	
CCl ₄	0.020	CBr ₄	HCl ₃	[PhBr]/[PhI]		k_{Br}/k_{HCl_3}	
		0.0704	0.0732	0.427 ^e	0.420 ± 0.013 ^e	0.42 ± 0.02	
CCl ₄	0.020	HCBBr ₃	CCl ₄	[PhCl]/[PhBr]		k_{HCBBr_3}/k_{Cl}	
		0.0513	10.2	1.81 ^e	128 ± 3 ^e	128 ± 3	
Benzene	0.044	BrCCl ₃	<i>i</i> -PrI	[PhBr]/[PhI]		$k_{Br'}/k_{I'}$	
		0.163	0.229	1.28	1.79	1.75 ± 0.03	
CCl ₄	0.066	0.142	0.200	1.21	1.72		
		0.021	0.0900	0.198	0.71 ^e	1.57 ± 0.06 ^e	1.57 ± 0.06
CCl ₄	0.0195	CBr ₄	CCl ₄	[PhBr]/[PhCl]		k_{Br}/k_{Cl}	
		0.0375	10.2	6.07	1650	1586 ± 60 ^g	
		0.020	10.2	3.54 ^e	1590 ± 37 ^e		
0.020	0.080	10.2	12.14 ^e	1550 ± 14 ^e			
CCl ₄	0.0196	BrCCl ₃	CCl ₄	[PhCl]/[PhBr]		$k_{Br'}/k_{Cl}$	
		0.0911	10.2	0.285 ^e	397 ± 7 ^e	500 ± 40 ^e	
0.021	0.0900	10.2	0.23 ^e				
CCl ₄	0.0216	<i>i</i> -PrI	CCl ₄	[PhCl]/[PhI]		$k_{I'}/k_{Cl}$	
		0.0868	10.2	0.345 ^e	347 ± 30 ^e	343 ± 25	
		0.0202	9.8	0.059	358 ± 15 ^e		
0.021	0.198	10.1	0.16 ^e	324 ± 5 ^e			
PhCl	0.0210	<i>p</i> -MeC ₆ H ₄ SH	CBr ₄	[PhH]/[PhBr]		k_{RSH}/k_{Br}	
		0.181	0.116	0.750	0.456		
PhCl	0.0257	PhCH ₂ SH	CBr ₄	[PhH]/[PhBr]		k_{RSH}/k_{Br}	
		0.1052	0.0967	0.375	0.298	0.291 ± 0.007	
	0.0251	0.1952	0.1053	0.590	0.284		

^a Cf. text for rate constant symbolism. ^b Concentration of C-H bonds. ^c Chlorobiphenyls. ^d Mean of three runs. ^e Mean of two runs. ^f Reference 8b reports 1.31. ^g Probably ~1500 ± 100; cf. text.

can be equated to k_H . Any and all rate constants related to k_H via competition kinetics can then be calculated.

We calculated k_H^{app} using yields of benzene and halobenzenes measured in mixtures of chlorobenzene and mineral oil. The rate constant k' was calculated via the von Smoluchowski equation,²⁵ in the form of eq 15

$$k' = 4\pi N(D_A + D_B)(r_A + r_B)/10^3 \quad (15)$$

where r = radius of species A or B, known to be valid at low viscosities to less than a factor of three. The required diffusion coefficients D were calculated from the equation of Wilke and Chang²⁶ (eq 16),

$$D = 7.4 \times 10^{-8}[(\phi M)^{1/2} T / \eta V^{0.6}] \quad (16)$$

where M = molecular weight of solvent, V = molal volume of solute of its normal boiling point, and ϕ = solvent "association parameter" (assumed to be 1.0). Equation 16 is reported to correlate D values with ~20% accuracy and to apply at elevated viscosities.^{1b}

After k_H had been established, the actual values of k_1 and k_{Br} were calculated at each mineral oil concentration via eq 17

$$k_X^{app} = k_H \left(\frac{\text{yield of PhX}}{\text{yield of PhH}} \right) \left(\frac{[C-H]}{[\text{scavenger}]} \right) \quad (17)$$

which is analogous to eq 14. In both equations [C-H] is the molar concentration of C-H bonds, which are assumed to be secondary in mineral oil. The small, unknown number of primary C-H bonds was neglected; tertiary C-H bonds were assumed to be absent, since no corresponding absorption was detected in neat mineral oil by 100-MHz ^1H NMR.²⁷ That mineral oil and cyclohexane show identical reactivities per C-H bond (cf. Table XII) further justifies this assumption.

Tables X and XI and Figure 3 present the results for I_2 and CBr_4 at 45 °C. All three sets of data reveal plateaus at higher viscosities; that for the second set with CBr_4 persists from 12 to 20 cP. For I_2 the first plateau is succeeded by a falloff of $k_{\text{H}}^{\text{app}}$ above about 10 cP, or 86.7% mineral oil. This the region in which the competition ratio k_1/k_{Br} increased, as a result of accumulation of secondary alkyl iodide. In the present experiment, this will artificially raise the iodobenzene yield and lower $k_{\text{H}}^{\text{app}}$. The first iodine plateau yields a value of $k_{\text{H}}^{\text{app}}$ very similar to that from the second CBr_4 run: omitting the first CBr_4 run because the plateau is too short, the values are 3.01 and $3.52 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; the mean is 3.26×10^5 ; and the deviation from the mean is $\pm 0.25 \times 10^5$, ~8%. In addition, the maximum deviations of the benzene and halobenzene yields are about $\pm 12\%$. We therefore report k_{H} as $3.3 \pm 0.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 45 °C referred, as noted, to the concentration of C-H bonds.

Experiments of the above type were not attempted with our other scavengers BrCCl_3 and isopropyl iodide. Their reactivities in benzene were much lower than those of I_2 and CBr_4 : $k_{\text{Br}}/k_1' = 6.0$ and $k_{\text{Br}}/k_{\text{Br}}' = 3.4$ (from the former ratio and $k_{\text{Br}}'/k_1' = 1.75$); cf. Table XII, and eq 9 and 10. Diffusion control would be reached at such a high mineral oil concentration that the plateau might not be clearly evident and the plateau value of $k_{\text{H}}^{\text{app}}$ uncertain. We have recently found, however, that $k_{\text{Br}}/k_{\text{HCl}_3} = 0.43$, indicating iodoform to be suitable. The discovery of additional reactive scavengers to which to apply this method is desirable.

Relative Rate Constants. We have utilized competition experiments to determine relative rate constants for a variety of phenyl radical reactions at 45 °C, with the end in view of calculating absolute rate constants for the substrates involved. The reactions include aromatic phenylations and halogen atom transfers; the results appear in Table XII. In addition, many relative rates have been reported in the literature, many of these at 60 rather than 45 °C. Because of the small temperature difference and the likelihood of very small ΔE_a values, these determinations were not repeated at 45 °C.

A few direct comparisons with previous reports are possible. (a) Our relative rate for chlorobenzene vs. benzene is $k_{\text{PhCl}}/k_{\text{PhH}} = 1.28 \pm 0.03$; Augood, Hey and Williams^{8b} report the value 1.31, identical within experimental error. The total yield of biphenyls (cf. Table XII) is only 71%, while, for several other determinations, total yields ranged up to 100%. The ratio which we have reported as $k_{\text{ortho}}/k_{\text{para}} = 1.68 \pm 0.07$ is probably to be compared with $k_{\text{ortho}}/k_{(\text{meta} + \text{para})} = 64/36 = 1.78$, in good agreement. (b) For bromotrichloromethane and isopropyl iodide, $k_{\text{Br}}'/k_1' = 1.75$ (in benzene), or 1.57 (in CCl_4); Danen and Winter report 1.72 in BrCCl_3 .^{24b} (c) For both thiophenol and thio-*p*-cresol in chlorobenzene, $k_{\text{RSH}}/k_{\text{Br}} = 0.45$. Denisov^{3d} quotes the value 518 for $k_{\text{PhSH}}/k_{\text{Cl}}$ (presumably in CCl_4), from which $k_{\text{PhSH}}/k_{\text{Br}} = 0.35$.

Our value for the ratio $k_{\text{H}}/k_{\text{Cl}}$, 0.055 (found by combining $k_{\text{H}}/k_{\text{PhCl}}$, $k_{\text{PhCl}}/k_{\text{PhH}}$, and $k_{\text{Cl}}/k_{\text{PhH}}$) agrees poorly with Bridger and Russell's⁷ value of 0.090, determined by direct competition between cyclohexane and CCl_4 . The error must stem from $k_{\text{Cl}}/k_{\text{PhH}}$ and $k_{\text{H}}/k_{\text{PhCl}}$, since $k_{\text{PhCl}}/k_{\text{PhH}}$ is in agreement with the literature value. We can therefore use these relative rates only for rough estimates of k_{PhH} and k_{PhCl} .

The reproducibility of most of the other relative rates is good. For k_{Br}/k_1' , however, values of 6.85 and 4.85 were ob-

tained by two different coworkers at different times; the weighted mean of 6.18 has been rounded to 6.0 for calculation of absolute rate constants. For $k_{\text{Br}}'/k_{\text{Cl}}$ a single worker obtained values of ~400 and 500 in separate, duplicate runs.

Alternative estimates of $k_{\text{Br}}/k_{\text{Cl}}$ are in fairly good agreement as follows: (a) direct determination via CBr_4 in CCl_4 , 1585; (b) $k_{\text{Br}}/k_1' \times k_1'/k_{\text{Cl}} = 4.2 \times 343 = 1400$; (c) $k_{\text{Br}}/k_1' \times k_1'/k_{\text{Br}}' \times k_{\text{Br}}'/k_{\text{Cl}} = 4.2 \times 1/1.57 \times 450 = 1260$; (d) Same as (c) with $k_{\text{Br}}'/k_{\text{Cl}} = 500, 1400$. We are adopting the value of 1500 ± 100 . Our decision not to apply a correction to the CBr_4 concentration should be borne in mind.

Additional Absolute Rate Constants. Table XIII records values of absolute rate constants, each calculated from one relative and one absolute rate constant, beginning with $k_{\text{H}} = 3.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. In reading the table, it should be remembered that k_{H} , or k_{sec} , is the statistically corrected value *per C-H bond*, so that it may be applied to any substrate with unperturbed secondary C-H bonds simply by multiplying by the number of such bonds. The rate constants for CCl_4 , CBr_4 , I_2 , and O_2 have not been statistically corrected, but apply *per molecule*, since each molecule displays unique reactivity. Table XIII contains several values based on relative rates at 60 °C, as justified above.

For several rate constants more than one method of calculation is possible; k_{Cl} , k_{Br} , and k_1 were each calculated in three different ways. (1) k_{Cl} is obtained from k_{H} via our indirect value of 0.055 for $k_{\text{H}}/k_{\text{Cl}}$ (vide supra); k_{Br} and k_1 can then be obtained from $k_{\text{Br}}/k_{\text{Cl}}$ and k_1/k_{Br} (Table XIII); this method is not used in general for the reasons given above, but a value of k_{Cl} is included to demonstrate the lack of agreement with methods 2 and 3. (2) k_{Cl} is obtained from k_{H} and Bridger and Russell's value of 0.090 (per C-H bond) for $k_{\text{H}}/k_{\text{Cl}}$; k_{Br} and k_1 are then calculated as in method 1. (3) k_{Br} and k_1 are obtained from the low viscosity points of the experiments used to determine k_{H} ; k_{Cl} is then obtained from $k_{\text{Br}}/k_{\text{Cl}}$. Method 3 required extrapolation of k_{Br} and k_1 , presented in Tables X and XI, to $\eta = 0.597$ cP (100% chlorobenzene). This was accomplished via plots of $1/k_{\text{obsd}}$ vs. η , which were found to be linear; the justification of this procedure is included in the Appendix. In these cases, $k_{\text{Br}}/k_{\text{H}}$ and k_1/k_{H} were obtained from k_{Br} and k_1 , not vice versa. Unfortunately, this method gives $k_1/k_{\text{Br}} = 3.85$, not in good agreement with the measured value of 2.08 (Table XII) nor 2.32 or 2.82 (Table VI). Correcting the low viscosity points for depletion of CBr_4 raises k_{Br} above 5.0×10^9 , and lowers k_1/k_{Br} to ~3.0.

The maximum deviation of results of methods 2 and 3 from their mean is 15% or less; that of k_1' is 24%, causing us to suspect the value 0.83×10^9 and therefore the value of 6.0 for k_{Br}/k_1' .

Discussion

The results of this study are briefly as follows. Certain scavenging reactions of phenyl radicals are nearly diffusion controlled at low viscosities, and therefore are truly diffusion controlled at elevated viscosities. This is evidenced by the approach to unity with increasing viscosity of relative rates for pairs of scavengers. Competitions between a diffusion controlled (scavenging) reaction and a slower reaction at high viscosities may be employed to calculate absolute rate constants of phenyl radical reactions, given a valid method of calculating diffusion controlled rate constants.

Because of the novelty of our method of calculating k_{H} , it is worthwhile to discuss its validity with some care. We shall then compare our rate constants with previous estimates and point out their implications.

Efficient Scavenging of Phenyl at High Viscosities. We have asserted that the highly efficient scavenging at all viscosities of phenyl radicals from PAT demonstrates the *virtual* absence of a cage effect. Two alternative explanations, neither one

Table XIII. Absolute Rate Constants of Phenyl Radical Reactions at 45 °C

Substrate	Reaction	Solvent ^a	Source		k , M ⁻¹ s ⁻¹
			Relative rate ^b	Rate constant ^c	
Secondary C-H, aliphatic	H transfer	Mineral oil-PhCl	Cf. text	Cf. text	$k_H = 3.3 \times 10^5$
Primary C-H, aliphatic	H transfer	CCl ₄	$k_{sec}/k_{prim} = 9.3^{d,e}$	$k_{sec} = k_H$	$k_{prim} = 0.35 \times 10^5$
Tertiary C-H, aliphatic	H transfer	CCl ₄	$k_{tert}/k_{sec} = 4.8^{d,e}$	$k_{sec} = k_H$	$k_{tert} = 16.0 \times 10^5$
Primary C-H, benzyl	H transfer	CCl ₄	$k_{prim-b}/k_{sec} = 1.00^{d,e}$	$k_{sec} = k_H$	$k_{prim} = 3.3 \times 10^5$
Ph-SH	H transfer	CCl ₄	$k_{PhSH}/k_H = 5800^{d,e}$	k_H	$k_{PhSH} = 1.9 \times 10^9$
PhCl	Addition	PhCl-c-C ₆ H ₁₂ or -mineral oil	$k_H/k_{PhCl} = 0.250$	k_H	$k_{PhCl} = 13.2 \times 10^5$
PhH	Addition	PhH-PhCl	$k_{PhCl}/k_{PhH} = 1.28$	k_{PhCl}	$k_{PhH} = 10.3 \times 10^5$
CCl ₄	Cl transfer	PhH-CCl ₄	$k_{Cl}/k_{PhH} = 5.6$	k_{PhH}	$k_{Cl} = 58 \times 10^5$
CCl ₄	Cl transfer	CCl ₄ -c-C ₆ H ₁₂	$k_H/k_{Cl} = 0.090^{d,e}$	k_H	$k_{Cl} = 37 \times 10^5$
CCl ₄	Cl transfer	CCl ₄	$k_{Br}/k_{Cl} = 1500$	$k_{Br} = 4.0 \times 10^9$	$k_{Cl} = 27 \times 10^5$
CCl ₄	Cl transfer	CCl ₄	$k_{Br}/k_{Cl} = 1500$	$k_{Br} = 5.0 \times 10^9$	$k_{Cl} = 33 \times 10^5$
CBr ₄	Br transfer	PhCl	$k_{Br}/k_H = 12\ 100$	k_H	$k_{Br} = 4.0 \times 10^9$
CBr ₄	Br transfer	PhCl	$k_{Br}/k_H = 15\ 200$	k_H	$k_{Br} = 5.0 \times 10^9$
CBr ₄	Br transfer	CCl ₄	$k_{Br}/k_{Cl} = 1500$	$k_{Cl} = 37 \times 10^5$	$k_{Br} = 5.5 \times 10^9$
I ₂	I transfer	PhCl	$k_I/k_H = 46\ 700$	k_H	$k_I = 15.4 \times 10^9$
I ₂	I transfer	PhH	$k_I/k_{Br} = 2.08$	$k_{Br} = 5.5 \times 10^9$	$k_I = 11.5 \times 10^9$
<i>i</i> -PrI	I transfer	PhH	$k_{Br}/k_I' = 6.0$	$k_{Br} = 5.0 \times 10^9$	$k_I' = 0.83 \times 10^9$
<i>i</i> -PrI	I transfer	CCl ₄	$k_{Br}/k_I' = 4.2$	$k_{Br} = 5.0 \times 10^9$	$k_I' = 1.19 \times 10^9$
<i>i</i> -PrI	I transfer	CCl ₄	$k_I'/k_{Cl} = 343$	$k_{Cl} = 37 \times 10^5$	$k_I' = 1.27 \times 10^9$
BrCCl ₃	Br transfer	PhH	$k_{Br}'/k_I' = 1.75$	$k_I' = 0.83 \times 10^9$	$k_{Br}' = 1.45 \times 10^9$
BrCCl ₃	Br transfer	CCl ₄	$k_{Br}'/k_I' = 1.57$	$k_I' = 1.23 \times 10^9$	$k_{Br}' = 1.93 \times 10^9$
BrCCl ₃	Br transfer	CCl ₄	$k_{Br}'/k_{Cl} = 450$	$k_{Cl} = 37 \times 10^5$	$k_{Br}' = 1.67 \times 10^9$
BrCCl ₃	Br transfer	CCl ₄	$k_{Br}'/k_{Cl} = 500$	$k_{Cl} = 37 \times 10^5$	$k_{Br}' = 1.85 \times 10^9$
O ₂	Addition	CCl ₄	$k_{O_2}/k_{Cl} = 1200^{e,f}$	$k_{Cl} = 37 \times 10^5$	$k_{O_2} = 4.4 \times 10^9$
O ₂	Addition	c-C ₆ H ₁₂	$k_{O_2}/k_H = 14\ 400^{e,f}$	k_H	$k_{O_2} = 4.7 \times 10^9$
(MeO) ₂ P(O)H, DMP	H-transfer	CCl ₄	$k_{DMP}/k_{Cl} = 2.85^{e,g}$	$k_{Cl} = 37 \times 10^5$	$k_{DMP} = 1.05 \times 10^7$
(MeO) ₃ P, TMP	Addition	TMP-DMP	$k_{TMP}/k_{DMP} = 33.1^{e,g}$	$k_{DMP} = 1.1 \times 10^7$	$k_{TMP} = 3.5 \times 10^8$

^a Solvent for relative rate determination. ^b From Table XII unless otherwise noted. ^c This table. ^d Reference 7. ^e At 60 °C; relative rates assumed similar at 45 °C, if ΔE_a is small. ^f Reference 6. ^g Reference 4b.

Table XIV. Rate Constants for PAT Decomposition^a in Presence and Absence of Scavengers in Benzene at 45 °C

Scavenger	10 ⁻⁵ k_{obsd} , s ⁻¹
None	8.06 ± 0.79
CBr ₄ , 0.5 M	7.02 ± 0.81
I ₂ , 0.2 M	8.06 ± 1.18

^a [PAT]₀, 0.020 M.

satisfactory, suggest themselves. First, the concentrated scavenger might trap geminate radicals, thus preventing the cage effect from increasing. However, Waits and Hammond²³ showed that concentrations of 0.5–1.0 M I₂ are required for up to ~50% cage scavenging of 1-cyanocyclohexyl radicals in chlorobenzene, and other reports must be interpreted similarly.¹⁶ At higher viscosities, scavenging efficiencies would still decrease. Our highest I₂ concentration was only ~0.2 M. On this basis, it is untenable that cage scavenging is responsible for the high efficiencies observed. A hidden issue here is whether the rate constant for I₂ and 1-cyanocyclohexyl radicals is also diffusion controlled; this is not yet known.

A second alternative is that the scavengers form charge transfer (CT) complexes with PAT, the concentrations of which would then increase with scavenger concentration. The probability that a scavenger molecule would be present at the moment of PAT decomposition would be increased. We have tried unsuccessfully to detect CT complexes, finding that (a) the rate of decomposition of PAT is unchanged by either CBr₄ (0.5 M) or I₂ (0.2 M) in benzene (cf. Table XIV), and (b) the UV-vis spectra of neither PAT nor I₂ are shifted or intensified, nor are any new bands observable.

If, then, a cage effect is virtually absent, it follows that inefficient scavenging in the more viscous of two equally reactive solvents is caused by a decrease in the scavenging rate constant by elevated viscosity, as discussed earlier.

The manipulation of this effect for measurement of the rate constant k_H requires a reliable means of calculating k_I and k_{Br} . The method adopted, i.e., the combined von Smoluchowski and Wilke-Chang equation, *probably* gives a precision of about ±50%, as an optimistic estimate. The Wilke-Chang equation (by which diffusion coefficients are calculated) is reported to be highly precise at elevated as well as ordinary viscosities.^{1b}

The von Smoluchowski equation, however, in the form of eq 18

$$k' = 4\pi\rho DN \times 10^{-3} / [(1 + 4\pi\rho DN \times 10^{-3}) / k_c] \quad (18)$$

has been tested only at low viscosities, employing the recombination of I atoms in CCl₄.^{25b} The diffusion coefficient $D(I)$ was measured via a new method, and was inexplicably large, some fivefold greater than $D(I_2)$. We are baffled by this discrepancy, and can only believe the empirical value of $D(I)$ to be incorrect. If $D(I)$ is calculated via the Wilke-Chang equation, the result is within 50% of that obtained by substitution into the von Smoluchowski equation of the appropriate values of k' , ρ , and k_c employed by Noyes: cf. Appendix, part 2. On this basis the von Smoluchowski equation appears to predict with an accuracy of some ±50% the rate constant for I atom recombination in CCl₄.

The required test of the von Smoluchowski equation at elevated viscosities is the measurement of a very large rate constant over a range of viscosities, perhaps in mixtures of mineral oil or glycerol with chemically similar nonviscous solvents. Such a study has recently been carried out using the coupling/disproportionation of *tert*-butyl radicals.^{25c}

Solvent effects should not be forgotten as a potential source of error, since solvent variations are intrinsic to our method. Thus, k_H has had to be determined in ~90% mineral oil–10% chlorobenzene, while many relative rates *must* be determined in either benzene or CCl₄. Our experience suggests, however,

that solvent effects on phenyl radical selectivities are small. First, in Figure 3, the first plateau of the I₂ run extends from 4–10 cP, or from 50 to 87% mineral oil. Second, halogen atom transfer selectivities as shown in Table XV are virtually invariant with solvent. Finally, studies in progress show that phenyl radicals show the same selectivity between addition to styrene and Cl abstraction from CCl₄ in several solvents. Recent books^{3c,e} make no mention of solvent effects on phenyl radical reactions. In summary we are encouraged that the discrepancies among calculated rate constants are as small as they are, and that absolute rate constants are internally consistent.

Previous Estimates of Rate Constants. A few previous estimates of rate constants were alluded to in the beginning. All of these are large enough to be consistent with the failure of phenyl radicals to dimerize. On the other hand, all the estimates but one fall short of our values.

Packer et al.^{11d} have estimated the rate constant for H abstraction from methanol as $>1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (per molecule of methanol). They employed the pulsed radiolysis of methanol solutions of *p*-toluenediazonium fluoborate, which produced toluene, formaldehyde, N₂, and H⁺ via a radical-chain mechanism. From Bridger and Russell's⁷ ratio, $k_{\text{toluene}}/k_{\text{methanol}} = 2.0$, $k_{\text{toluene}} > 2.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, per molecule, or $\sim 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, per C–H bond, in fair agreement with our value. Ingold concluded^{11e} from the value of Packer et al. that k_{toluene} would be at least $10^6 \text{ M}^{-1} \text{ s}^{-1}$, presumably per molecule, or $3.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, per C–H bond, in exact, if fortuitous, agreement with our value.

Duncan and Trotman-Dickenson^{12a} generated phenyl radicals by photolysis of acetophenone vapor. Their analysis of the kinetics of consumption of added isobutane led to the following data at 333 °C, for reaction of phenyl with isobutane: $E_a = 6.7 \text{ kcal mol}^{-1}$, $\log A = 8.8$, and $\log k = 6.4$, the last two based on the units $\text{M}^{-1} \text{ s}^{-1}$. From these it follows that k at 45 °C is $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, while from the present work k_{tert} is $1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, or 100 times greater. This discrepancy can only partially be due to the long, nearly 300 °C, extrapolation of k and the effect of uncertainty of E_a and A on the result. Decreasing $\log A$ to 7.8 and E_a to 3.9 kcal mol⁻¹ (consistent with $\log k = 6.4$ at 333 °C) leads to $k = 1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 45 °C. On the other hand, a tenfold error in our value appears highly unlikely. This is the most disturbing discrepancy with our results. We are reluctant to suggest that Duncan and Trotman-Dickenson's analysis is incorrect, but do not see any viable alternative.

MacLachlan and McCarthy^{11a} estimated k_{PhCl} as $4.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at ambient temperature, based on product yields in pulsed radiolysis of chlorobenzene. They assumed that biphenyl arose from dimerization of phenyl radicals, estimated to peak at $\sim 4 \times 10^{-4} \text{ M}$, and assigned this process the rate constant $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This is the same value as calculated^{11a} for second-order decay of optically absorbing radicals, postulated to be substituted cyclohexadienyl radicals; it is the smallest of the five values reported by factors of 3 to 24. From product yields, phenyl radical addition to chlorobenzene was inferred to be four times as fast as dimerization. "Ipso" attack on chlorobenzene, leading to biphenyl, was not considered. Given these uncertainties, the discrepancy of ~ 20 -fold between their value and our rough one can probably be explained away. Indeed, adoption of $k = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for dimerization would increase k_{PhCl} by tenfold, giving much better agreement. DeTar's observation,^{11c} that perhaps the elements of this system have not been correctly identified, should be borne in mind.

Starnes^{11b} has provided three estimates of k_{O_2} for phenyl radicals: these are 2.4, 6.2, and $26 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The largest of these is still 18 times smaller than our estimate. For two of these, Starnes used MacLachlan and McCarthy's value of

Table XV. Solvent Effects on Halogen Atom Transfer Selectivities at 45 °C

Solvent	$k_{\text{Br}'} / k_1'^a$	$k_{\text{Br}} / k_1'^a$
Cyclohexane	1.47	4.8
Benzene	1.77	6.0
CCl ₄	1.71	5.3
Acetonitrile	1.51	6.4

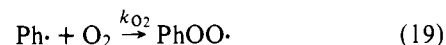
^a Toward phenyl radicals from PAT; cf. text for symbolism; k_1' refers to 2-iodobutane rather than 2-iodopropane; [PAT]₀, 0.02 M; [BrCCl₃]₀, [CBr₄]₀, and [2-iodobutane]₀, 0.14–0.20 M.

k_{PhCl} , while for the third he extrapolated Duncan and Trotman-Dickenson's value. The first, smallest value can be disregarded, since it utilized an incorrect value of $k_{\text{O}_2} / k_{\text{PhH}}$ in the range 540–970, rather than ~ 4000 .

Finally, DeTar^{11c} has estimated values of k_{H} and k_{PhH} as part of the monumental task of accounting for all products of benzoyl peroxide decomposition in benzene at 80 °C. His value of $k_{\text{H}} = 5 \times 10^4$ is not much less than ours, but $k_{\text{PhH}} = 2 \times 10^3$ is low by nearly three orders of magnitude. The chief cause is certainly the assumption of low values for rate constants of radical-radical reactions, e.g., 1×10^8 for alkyl-alkyl combination, for which values of 0.4 to $\sim 3 \times 10^9$ have recently been measured.^{9,16} Indeed, several radical coupling reactions have been observed as cage processes, implying bulk rate constants of $\sim 1 \times 10^9$.¹⁶

Implications of Rate Constants. It is now possible to discuss the reactivity of phenyl radical with more confidence than previously. First, the high value of k_{H} supports the conclusion which others have reached,^{11c} that phenyl radicals do not normally dimerize in solution because their steady-state concentration is kept low by rapid reaction with solvent. This is as true in aromatic solvents ($k_{\text{PhH}} 1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) as in aliphatic ones. In this respect phenyl resembles *tert*-butoxy.

We may now explain the anomalous behavior of phenyl radicals toward dioxygen, normally an excellent scavenger of carbon radicals, both alkyl and aralkyl.



Russell and Bridger⁶ reported the rate ratio 1200 for $k_{\text{O}_2} / k_{\text{Cl}}$, corresponding to $k_{\text{O}_2} / k_{\text{H}} = 1.4 \times 10^4$; on the other hand, they estimated values of $k_{\text{O}_2} / k_{\text{H}}$ for aralkyl radicals up to 10^{10} . The inefficient scavenging of phenyl radicals by dioxygen had been explained by Eberhardt and Eliel²⁸ and subsequently DeTar^{11c} by the rapid reaction of phenyl radicals with the solvent. Russell and Bridger⁶ and Simamura et al.,²⁹ however, postulated that reaction¹⁹ is abnormally slow because of an adverse polar effect, both reactants being acceptors. Our value of $k_{\text{O}_2} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is consistent only with the former explanation. Although dioxygen is a "diffusion limited scavenger" toward phenyl, it cannot compete with solvents except as higher pressures increase its solubility. At higher viscosities, dioxygen should behave like I₂ and CBr₄ in competing more poorly for phenyl vis-à-vis the solvent.

Selectivity vs. Reactivity. Close examination of the selectivity and reactivity of phenyl in comparison with other radicals is of considerable interest. It has frequently been asserted that greater selectivity implies lesser reactivity³⁰ and such a relationship has been amply demonstrated for electrophilic aromatic substitution^{30b} and argued for H abstraction by several radicals.^{3b} More recently, however, it has been recognized that adherence to the relationship is only to be expected for series of closely related reactions. We wish to emphasize that, in contrast to electrophilic aromatic substitution, reactions of several small radicals, including phenyl, do not show a clear selectivity-reactivity relationship.

Table XVI. Selectivities and Reactivities of Small Radicals

Radical	$k_{\text{tert}}/k_{\text{prim}}$ at 60 °C ^a		$k, M^{-1} s^{-1}$, per molecule, at 40–45 °C						
	Alkyl	Benzyl	Toluene	CH ₃ OH	CCl ₄	CH ₂ =CH ₂	(CH ₂ =CH-) ₂	I ₂	O ₂
CF ₃		24.8 ^b	3 × 10 ⁴ ^c	8 × 10 ³ ^{d,e}					
CH ₃	75 ^f	12.9	3 × 10 ² ^a	2 × 10 ² ^a	4 × 10 ² ^a	5 × 10 ³ ^{d,e}	1 × 10 ⁶ ^{d,e}	6 × 10 ⁹ ^{d,e}	5 × 10 ⁹ ^{d,e}
C ₆ H ₅	44	9.7	1 × 10 ⁶	5 × 10 ⁵ ^g	4 × 10 ⁶	8 × 10 ⁶ ^{g,h}	1 × 10 ⁸ ^{g,i}	1 × 10 ¹⁰	5 × 10 ⁹
<i>t</i> -C ₄ H ₉ O	44 ^j	6.8 ^j	1 × 10 ⁵ ^{d,k}						

^a Cited in ref 3b. ^b Reference 31b. ^c Reference 3d. ^d At 25 °C. ^e Reference 31a. ^f Extrapolated from value of 50 at 182 °C assuming $\Delta E_a = 1.0$ kcal/mol. ^g Via relative rates in ref 6a or 7; ref 11d estimates $k \geq 1.4 \times 10^5$ at 25 °C. ^h Propene. ⁱ Penta-1,3-diene. ^j At 40 °C. ^k Reference 10b.

Table XVII. Reactivity vs. Selectivity of some Radicals toward CX₄, RSH, and PhCH₂R at 60 °C

Radical	$k_{\text{CBr}_4}, M^{-1} s^{-1}$ ^a	$k_{\text{CBr}_4}/k_{\text{CCl}_4}$ ^a	$k_{\text{CBr}_4}/k_{n\text{-RSH}}$ ^a	$k_{\text{PhEt}}/k_{\text{PhMe}}$ ^{a,b}
Polystyryl	2.0 × 10 ²	151	0.062 ^c	5.4
Poly(methyl methacrylate)	2.4 × 10 ²	1370	0.50 ^c	2.6
Poly(methyl acrylate)	8.6 × 10 ²	3300	0.25 ^c	
Poly(vinyl acetate)	1.0 × 10 ⁵	40	~1 ^c	2.6
Phenyl	5.0 × 10 ⁹ ^d	1500 ^d	~3.4 ^{d,e}	3.1 ^f

^a Reference 32. ^b Not statistically corrected; i.e., *ks* are per molecule. ^c With *n*-butanethiol. ^d This work, 45 °C; cf. Tables XII and XIII. ^e With α -toluenethiol. ^f Reference 7.

Table XVI compares some rate constants and selectivities for several radicals, listed in order of decreasing selectivity. Reactivities do not, however, increase smoothly from top to bottom. As Szwarc et al.^{31b} have noted, the more reactive CF₃ radical is far more selective than CH₃. *tert*-Butoxy, the least selective, is slightly *less* reactive than phenyl and negligibly more reactive than CF₃. The very large reactivity difference between phenyl and methyl, toward all substrates except I₂ and O₂, suggests a larger difference in selectivity than is found. For these four radicals, then, reactivities and selectivities are somewhat scrambled and have little predictive value.

Another anomaly is found in comparing phenyl with polystyryl and other polymer radicals, as in Table XVII. Although the reaction of phenyl with CBr₄ is diffusion controlled, its selectivity toward CBr₄ as compared with CCl₄ is at least ten times *greater* than that of two of the four polymer radicals listed. No general selectivity–reactivity relationship is followed even with the polymer systems. The selectivity of phenyl toward ethylbenzene and toluene is 4.6 at 60 °C; those of the polymer radicals mentioned above, all many orders of magnitude less reactive than phenyl, range from 2.6 to 6.0,³² again flouting the selectivity–reactivity relationship.

Experimental Section

All solvents and scavengers were reagent grade materials and their boiling or melting points conformed to reported values. Isopropyl iodide was distilled twice, the fraction of bp 82–83 °C being used; bromotrchloromethane was also distilled twice, bp 100–101.5 °C. Mineral oil was pharmaceutical grade “Nujol”.

Phenylazotriphenylmethane (PAT). This was prepared by essentially the method of Cohen and Wang.³³ A solution of triphenylchloromethane (84 g, 0.30 mol) and phenylhydrazine (70 g, 0.65 mol) in 2 L of anhydrous ether, in a round-bottomed flask fitted with reflux condenser, was refluxed for ~1.5 h. The reaction mixture was cooled to room temperature, the precipitated phenylhydrazine hydrochloride filtered off, and the solution evaporated to dryness. The additional phenylhydrazine hydrochloride which precipitated during concentration of the ether solution was removed by mixing the entire residue with 300 mL of benzene and filtering. The filtrate, containing *N*-phenyl-*N'*-triphenylmethylhydrazine, was concentrated to remove most of the benzene.

To the resulting slurry dissolved in 400 mL of ether was added 400 mL of saturated sodium bicarbonate solution and 75 mL of 30% hydrogen peroxide, and the two-phase mixture was stirred at room temperature for ~10 h. On a few occasions when the oxidation failed to proceed, it was found to be catalyzed by a few milliliters of aqueous

0.1 N copper(II) sulfate. The ether phase was separated and shaken with four 200-mL portions of aqueous 5% sodium hydroxide solution and then washed with three–four 100-mL portions of water (until the washings were no longer basic to phenolphthalein). The ether phase was filtered through anhydrous sodium sulfate, filtered again, and concentrated to dryness. The crude solid was recrystallized by dissolving it in 150 mL of dichloromethane, and adding 350 mL of absolute ethanol and allowing it to stand overnight in the refrigerator. The yield of recrystallized product of mp 108–109 °C (lit.⁷ 110–112 °C) was 36.5 g, 0.105 mol, 35.0% based on triphenylchloromethane.

Determination of Purity of PAT. 1. Nitrogen Evolution. The pressure of nitrogen evolved by decomposition of a weighed sample of PAT dissolved in toluene and collected in a known volume was measured. Samples of PAT in the range 0.5–2.0 g were dissolved in ~30 mL of toluene in a Claisen flask fitted with a breakseal and two standard taper joints and the solution was outgassed on the vacuum line by freeze–thaw cycles using liquid nitrogen. The flask was sealed, heated at 70 °C for 2 h, cooled, and attached to the vacuum line, and the seal broken to allow the flask contents to expand into a volume which had been previously measured and which contained a manometer. The vapor pressure of toluene was subtracted from the total pressure; the value of 13 Torr was used, obtained by extrapolating to zero weight of PAT a plot of pressure of N₂ vs. weight of PAT taken. Typical samples of PAT had purities ranging from 88 to 94.5%.

2. Spectrophotometry. A Cary Model 14 recording spectrophotometer was used to determine the absorbance of solutions of PAT in hexane at λ_{max} 420 nm (a second λ_{max} 263 nm was also observed, as reported by Burawoy³⁴). The molar absorptivity, as determined using batches of PAT which had been assayed by nitrogen evolution, was 204 ± 6, which is in good agreement with that reported by Kampmeier et al.,^{3b} 201 ± 1. Subsequent batches were assayed using a value of 204.

Coefficients of Viscosity of Solvent Systems. Viscosities were determined by means of an Ostwald viscometer placed in a water bath thermostated to ±0.10 °C. The outflow times for each solvent mixture and for water were determined, and then the viscosity of each solvent mixture was calculated by the equation

$$\eta_{\text{solv}} = \frac{(\eta_{\text{H}_2\text{O}})(\rho_{\text{solv}})(t_{\text{solv}})}{(\rho_{\text{H}_2\text{O}})(t_{\text{H}_2\text{O}})}$$

The results are presented in Tables II, III, IV, and XI.

Thermal Decomposition of PAT. General. All reactions were run in sealed glass ampules prepared from 18 × 150 mm Pyrex test tubes. A stock solution of PAT in the aromatic solvent, either benzene or chlorobenzene, was first prepared. To each test tube ampule was added the amounts of mineral oil and aromatic solvent required to give the desired volume percent mineral oil in the final reaction mixture. The

volume at this point was either 8.0, 9.0, or 9.5 mL, depending on whether the highest percentage of mineral oil desired was 80, 90, or 95%. Then an aliquot of the PAT stock solution, 2.0, 1.0, or 0.5 mL, was added to give a total volume of 10.0 mL. The concentration of the PAT in the stock had been set so that this dilution would give the desired final concentration of PAT in the ampules. The ampules were then flushed with nitrogen, sealed using a torch, and placed in a thermostatically controlled water bath set at the desired decomposition temperature. The decomposition was allowed to proceed for about 20 half-lives.

Those scavengers which were liquids (bromotrichloromethane and isopropyl iodide) were added directly to the PAT stock solution. The solid scavengers (iodine and carbon tetrabromide) were first dissolved in the aromatic solvent–mineral oil mixture before addition of PAT stock solution, to prevent their precipitation, or that of PAT, from the stock solution.

Analysis of Reaction Mixtures by GLC. The following gas chromatographs were used at various times: F & M Model 700 with thermal conductivity detector and disk-chart integrator; F & M Model 810 with flame ionization detector; Aerograph Autoprep Model 700 with thermal conductivity detector. Columns and conditions used for various separations are shown in Table XVIII.

Analysis of most samples was performed by breaking the ampules and directly injecting the sample. Samples containing iodine were first treated with a few milliliters of water and 200–300 mg of either sodium thiosulfate or sodium bisulfite, and the ampules shaken to destroy the iodine. The GLC analysis was then performed on the organic phase.

Quantitative standards containing the anticipated products in the anticipated concentration range were prepared and injected immediately before and/or after the injections of decomposition samples. The standards were also made up with mineral oil for each volume percent used in an experiment. Only with the flame ionization detector was there any variation of detector response with changes in mineral oil concentration. This detector showed a response with 90% mineral oil that was only 82% of that in the absence of mineral oil.

Determination of Tetraphenylmethane as Decomposition Product. The procedure was adapted from that of Hey.³⁵ PAT (84% pure, 5.0 g), containing 0.012 mol of PAT, was combined with 40 mL of benzene in a 100-mL three-necked round-bottomed flask equipped with a magnetic stirring bar, two reflux condensers in series, thermometer, and nitrogen inlet. The flask was gradually heated at 1 °C/min to 80 °C. It was then refluxed under nitrogen for 2 h. The solution gradually colored to a dark red between 65 and 80 °C. The benzene was distilled from the flask, foaming being controlled by varying the nitrogen flow. The residual solution was transferred to a 10-mL pear-shaped flask set up for distillation. The apparatus was wrapped with asbestos and was heated with a Bunsen burner. Fraction I distilled at 260–310 °C, fraction II at 330–375 °C; both crystallized on cooling. Fraction II was dissolved in 20 mL of hot ethanol and filtered. The filtrate deposited a mixture of triphenylmethane and biphenyl. The original residue from filtering ethanolic fraction II was dissolved in 5 mL of boiling toluene and allowed to crystallize at 5 °C. The crystallized residue was collected and identified as tetraphenylmethane by mp 265–273 °C (lit.³⁶ 281–282 °C) and ¹H NMR in chloroform-*d* (singlet, δ 7.1 ppm). The yield was 0.11 g, 0.00034 mol, 2.9% of theory.

Rates of Decomposition of PAT at Different Viscosities. The decomposition was monitored spectrophotometrically via the decrease in absorbance at λ_{\max} 420 nm, using a Beckman DB spectrophotometer. A stock solution containing 1.532 g of PAT in 25.0 mL benzene was prepared, thus having a concentration of 0.176 M. Of this solution 1.0 mL was diluted with 9.0 mL of a chlorobenzene–mineral oil mixture prepared so that the final solution would be either 30, 60, or 90 vol % mineral oil; a series of 0% mineral oil samples was also prepared. The tubes were sealed and placed in a water bath thermostated at 45 °C, and ampules were removed at intervals and quenched in ice. For analysis, the tubes were broken open, the contents were diluted to 50.0 mL with hexane, and the absorbance was determined. The first-order rate constants were calculated from the equation

$$k = (2.303/t) \log \frac{(A_0 - A_\infty)}{(A_t - A_\infty)}$$

The results appear in Table XIX.

Rates of Decomposition of PAT in Presence and Absence of Scavengers in Benzene at 45 °C. Rates were determined manometrically

Table XIX. Decomposition Rates of PAT in Chlorobenzene–Mineral Oil Mixtures at 45 °C

Mineral oil, vol %	Relative viscosity	k/k_0^a	$t_{1/2}$, h
0	1.0	1.0	2.60
30	1.73	0.86	3.03
60	4.04	0.76	3.40
90	21.2	0.67	3.91

^a Rate constant at given volume percent mineral oil divided by rate constant in pure chlorobenzene.

using a gas buret fitted with leveling bulb connected to the reaction vessel, a one-necked round-bottomed flask fitted with reflux condenser. The entire apparatus was filled with nitrogen and the solution had been purged with nitrogen prior to a run; a magnetic stirrer was used to prevent supersaturation of the solution with nitrogen. The PAT was introduced either (a) by dissolving it in the solvent and adding it to the flask, after which the solution was purged with nitrogen and allowed to equilibrate thermally for ~30 min; or (b) by adding PAT to the reaction flask, then adding deoxygenated, thermally pre-equilibrated solvent to the flask. Method b permitted a larger volume of the gas buret to be used. Volumes were read 10–15 times during a run and the rate constant calculated via

$$k = (2.303/t) \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

for each point, then the values averaged. The data are reported in Table XIV of the text.

UV-vis Spectra of PAT and Iodine in Hexane. *n*-Hexane was used as solvent to avoid absorbances and complexing characteristic of benzene. The spectrum of PAT + I₂, both at their maximum solubility of 0.016 M, was scanned vs. I₂ in *n*-hexane from 350 to 700 nm, and found to be identical with that of PAT in hexane vs. hexane. Similarly, the spectrum of PAT + I₂ vs. hexane alone in the range 235–350 nm was identical with that of PAT–hexane vs. hexane, which shows λ_{\max} 263 nm (ϵ 14 960)³⁴ and 420 (204). Iodine in hexane is transparent from 235 to 350 nm. These results indicate that PAT and I₂ form either a weak complex in hexane, or a complex with a small value of ϵ for the CT band, or both. For comparison, iodine in CCl₄ shows a single λ_{\max} 520 nm (ϵ 950), which is shifted to 498 nm in a donor solvent such as benzene, with the appearance of a new band at 290 nm (ϵ 9750);³⁷ for I₂ + benzene the formation constant is 0.16 in CCl₄.³⁸ For I₂ and pyridine the reported CT absorbance has λ_{\max} 237 nm (ϵ 51 700), and the formation constant is 132 in *n*-heptane.³⁹

Acknowledgments. We thank the U.S. Army Research Office—Durham (now the U.S. Army Research Office) for financial support of the work of R.G.K., and the Faculty Research and Creative Endeavors Committee of Central Michigan University for supporting the work of N.R.H.

Appendix

1. Extrapolation of Encounter-Controlled Rate Constants to Low Viscosities. A rate constant k_{obsd} may be expressed as fk' (cf. eq 6), where f is defined by eq 20

$$f = \frac{k_r}{k_r + k_d} \quad (20)$$

k_r is the rate constant for reaction of phenyl radical and scavenger molecule in encounter, and k_d , for their diffusive separation; k_d depends on $1/\eta$, while k_r is independent of η . According to the combined von Smoluchowski and Chang–Wilke equations, k' may be expressed as A/η (A = constant). It may be shown that $f = \eta/(c + \eta)$ (c = constant), by substituting $k_d = A/\eta$ into eq 20. We may then express k_{obsd} by eq 21

$$k_{\text{obsd}} = fk' = \frac{\eta}{c + \eta} \frac{A}{\eta} = \frac{A}{c + \eta} \quad (21)$$

It follows that

$$\frac{1}{k_{\text{obsd}}} = \frac{c}{A} + \frac{\eta}{A} \quad (22)$$

At any η , one may plot $1/k_{\text{obsd}}$ vs. η ; at high η , c/A may be neglected, and one may plot k_{obsd} vs. $1/\eta$.

2. To test the Wilke–Chang and von Smoluchowski equations (16 and 18, respectively; cf. text), the rate constant for iodine atom recombination in CCl_4 at 25 °C may be calculated, and compared with that measured.

Substitution into eq 16 of $\phi = 1.0$, $M = 142$ g/mol, $V \approx 35$ cm^3/mol , $T = 298$ K, $\eta = 0.906$ cP (note that for $\text{I}_2(\text{s})$ at 298 K, $V = 51.5$ cm^3/mol , from $\rho = 4.93$ g/ cm^3 and its molecular weight; at normal boiling point, assuming 30% expansion, $V = 67$ cm^3/mol) gives $D(\text{I}) = 3.4 \times 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$.

Substitution into eq 18 of this value and those employed by Noyes,^{25b} $\rho = 4.30 \times 10^{-8}$ cm and $k_c = 55.2 \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$, gives $k' = 9.3 \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$. The measured value^{25b} is 8.2×10^9 $\text{M}^{-1} \text{s}^{-1}$.

Use of the Stokes–Einstein equation in the form, $D = kT/4\pi\eta r$, $\eta = 9.06 \times 10^{-3}$ P, and $r = 1.37 \times 10^{-8}$ cm, gives $D(\text{I}) = 2.64 \times 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$, whence $k' = 7.4 \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$.

Supplementary Material Available: Competitions of scavengers for phenyl radicals over a range of viscosity (Tables VI and VII), viscosity vs. molecular weight for *n*-alkanes (Table VIII), calculated diffusion limited rate constants for phenyl radical–scavenger reactions (Table IX), and GLC columns and conditions (Table XVIII) (5 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Portions of this work have been presented at the First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 13–15, 1968, Abstract 194, and at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 22–27, 1970, Abstract ORGN 21. (b) Taken in part from the Ph.D. Thesis of R.G.K., Boston University, 1973.
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